

**The performance of Diesel Fuel manufactured by the Shell Middle Distillate
Synthesis process**

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Summary

The Shell Middle Distillate Synthesis (SMDS) process converts natural gas into diesel or kerosine via synthesis gas by combining a modern, improved Fisher-Tropsch synthesis and a special hydro-conversion process. The diesel cut has very good cetane quality, low density, plus negligible sulphur and aromatics contents; such properties make it potentially valuable as a diesel fuel with lower emissions than conventional automotive gas oil (AGO).

The performance of SMDS product as diesel fuel has been evaluated. Regulated emissions data from light-duty (LD) vehicles and heavy-duty (HD) engines representing both Euro I and Euro II technologies confirm considerable advantages for SMDS over current European AGO. Emission benefits are particularly high for LD vehicles with particulate matter, carbon monoxide and hydrocarbon emissions almost halved in some. Smaller, but significant, reductions in all four regulated emissions occur with HD engines. These emission benefits are similar to values predicted using fuel parameter models derived for conventional diesel fuels.

Although the straight-chain paraffinic nature of SMDS offers good biodegradability, it causes in-service problems. The cold flow performance of SMDS, together with low swelling characteristics in elastomeric seals, may limit its use to that of an AGO blending component. Loss in power and volumetric fuel consumption would be perceived on switching to SMDS from conventional AGO, however unsatisfactory fuel lubricity and lack of inherent antioxidancy can be overcome by additives.

1. OVERVIEW OF SMDS - PROCESS AND PRODUCTS

AGO derived from the Shell Middle Distillate Synthesis Process has unusual physical and chemical properties when compared with conventional AGOs. Since 1991 various research programmes have been designed and executed, in order to assess the use of SMDS as an AGO blending component. The results from these collective programmes are described below, focusing on those performance aspects of AGO anticipated to be affected by the unique properties of SMDS. The strengths and weaknesses of SMDS as a diesel fuel and associated in service performance are described.

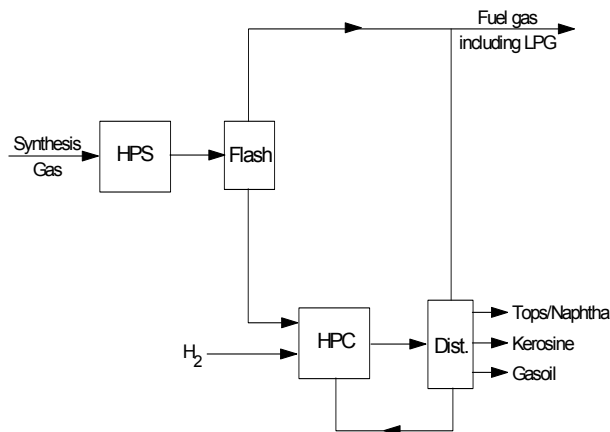


Figure 1. SMDS process - simplified flow scheme

The SMDS process outline is well documented(1) only a brief description is offered here, [Fig. 1](#). The process was developed at Shell Research & Technology Centre Amsterdam and comprises essentially of 3 stages:

1. Manufacture of synthesis gas (hydrogen + carbon monoxide - with a $H_2:CO$ ratio of approximately two) from natural gas by non-catalytic auto-thermal partial oxidation using, for example, the Shell Gasification Process.
2. Wax synthesis from $CO + H_2$ by Heavy Paraffin Synthesis (HPS), followed by flash distillation to separate light ends (e.g. LPG).
3. Cracking of wax to distillates by Heavy Paraffin Conversion (HPC), where the boiling range and quality of the products can be adjusted to produce either kerosine or gasoil.

The SMDS gasoil cut (150-350°C) has very good cetane quality (76-81 CN), low density (e.g. 770 kg/m³) and low sulphur and aromatics contents, which should make it potentially valuable for improved emissions performance from diesel vehicles. [Table 1](#) details the properties of SMDS and comparable AGO samples, *i.e.* a current reference CEN fuel (RF73) and a Swedish Class I (a very low sulphur content fuel).

SMDS is virtually paraffinic in nature (with a high proportion of straight-chain paraffins) and contains almost no aromatic, cycloparaffinic or polar species. This could give rise for concern in the areas of

elastomer compatibility, lubricity and peroxide formation.

Table 1. Typical SMDS and AGO sample analyses

Property	CEN AGO (RF73)	Swedish Class I	SMDS
DENSITY ^a @ 15°C kg/m ³	837	814	776
DISTILLATION, °C ^b			
IBP	201	197	184
10%	219	213	-
50%	269	231	275
90%	326	269	340
FBP	368	293	-
CETANE NUMBER	50	58	81
CETANE INDEX ^c	52.2	50.4	-
VISCOSITY @40°C cst ^d	2.823	1.903	2.702
SULPHUR, %m	0.05	0.001	<0.0002
AROMATICS, %m ^e			
Mono	25	9.7	<0.05
Di	2.1	0.1	<0.05
Tri	1.2	<0.05	<0.05
Total	28	10	<0.05

a. IP160/ASTM D1298, b. IP123/ASTM D86, c. IP380/94, d. IP71/ASTM D445, e. HPLC, IP391

2. ANTICIPATED PERFORMANCE OF SMDS AS A DIESEL FUEL

Increasing concerns over air quality have led to environmental legislation with more stringent limits for diesel light and heavy-duty vehicles. The four regulated emissions measured are particulate matter (PM), nitrogen oxides (NO_x), carbon monoxide (CO) and hydrocarbons (HC), which are measured using the appropriate test cycles stipulated in the European regulations:

- Heavy duty (HD) - R49 steady state test cycle
- Light duty (LD) combined ECE+EUDC test cycle

Regulated emissions data collected in-house has enabled the derivation of predictive emissions models based on fuel properties. Although there are differences in the way fuel composition affects emissions from LD vehicles and HD engines, it is possible to make some qualitative generalisations. A description of how emissions performance is expected to be affected by the distinctive properties of SMDS is given in [Table 2](#).

Table 2. Properties of SMDS against anticipated performance

Fuel Property	Performance Aspect
High Cetane	Low gaseous (CO, HC and NO _x) Low particulate emissions
Low Density	Low particulate emissions Lower power Higher fuel consumption per unit volume Lower fuel consumption per unit mass
High n-alkane content	Poor cold flow Good biodegradability
Low Aromatics	Possible elastomer compatibility problems
Low Sulphur	Low particulate emissions Indication of Poor lubricity Poor natural antioxidant
Low Polar Species	Poor lubricity Poor natural antioxidant

3. EMISSIONS PERFORMANCE

3.1. Quantification of emissions benefits

In-house emissions data for Euro-I (1992-1995) and Euro-II (1996-1999) vehicles and engines has been used to assess the emissions benefits in changing from a typical European fuel specification (RF73 as an example CEN fuel) to an SMDS AGO. The results are shown in [Table 3](#) and illustrated in [Fig 2](#) for Euro II.

Table 3. Emissions benefits for SMDS with respect to current CEN fuel

	Light-duty vehicles		Heavy-duty engines	
Benefit (%)	Euro I*	Euro II**	Euro I [†]	Euro II [‡]
PM	42	39	18	18
NO _x	10	5	16	15
HC	45	63	13	23
CO	40	53	22	5

* four IDI non catalyst (Ford Transit 2.5L, Ford Orion 1.8L, Peugeot 605 2.1L and Renault 21 2.1L),

** two DI + catalyst (Audi 80 1.9L and Audi 100 2.5L), one IDI + catalyst (VW Golf 1.9L) and one IDI non catalyst (Ford Orion 1.8L),

[†] Mercedes-Benz 6L OM366 calibrated to Euro I,

[‡] Mercedes-Benz 6L OM366 calibrated to Euro II.

Thus, for LD vehicles:-

- large (40%+) emission benefits are achievable by SMDS with both Euro I and Euro II IDI and DI technologies for PM, HC and CO.
- NO_x emissions are scarcely affected in LD vehicles (though this is technology dependent with the DI

vehicles showing no measurable change for SMDS and IDI ones a small benefit of ~10%).

Whereas for the Mercedes Benz 6L HD engine

- moderate (10-20%) emission benefits are achievable by SMDS with both Euro I and Euro II cycles for PM, HC and NOx.
- greater benefits for CO in Euro I than Euro II technology (*n.b.* both CO and HC emission levels are already well below the emission limits with the CEN fuel).

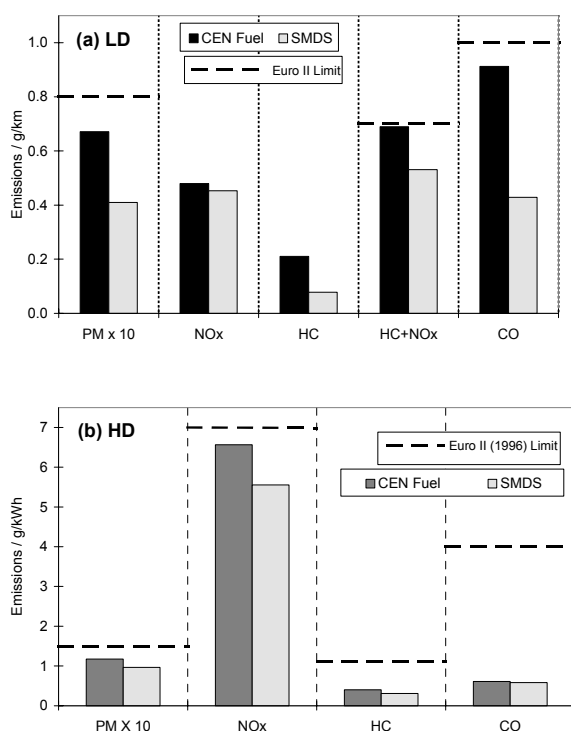


Figure 2. Regulated emissions levels for (a) the mean of four LD Euro II vehicles and (b) a 6L Mercedes HD Euro II engine fuelled with a CEN fuel and SMDS.

Euro II (1996)

(Limits are included as broken lines for comparison).

These SMDS benefits are dependent both on the exact vehicle or engines chosen for the comparison and the appropriate reference fuel. It is probable that these benefits will become smaller as new engine technology is introduced, particularly because the reference fuel in future will need to change to take account of EU 2000 specifications by having higher cetane number and lower density. By then (and later, as specifications tighten for 2005 and beyond) SMDS may become more attractive as a blending component to upgrade refinery stock to required cetane and density levels.

3.2. Emission Models (2-4)

The knowledge base on regulated emissions from a wide range of diesel fuels and vehicles has been used to derive fuel dependent emission models using standard statistical methods. The models contain two, three and four fuel properties as linear parameters, *e.g.* equation

(1) below illustrates a three parameter model for regulated emission (E):-

$$E = a + b.[\text{fuel property 1}] + c.[\text{fuel property 2}] + d.[\text{fuel property 3}] \quad (1)$$

where the fuel properties are any from:-

- density (ρ),
- cetane number (CN),
- viscosity (η),
- distillation temperature (T90),
- total aromatics (Ar),
- polyaromatics (PA), and
- sulphur.

The output from such models can be used to predict the effect of changing fuel quality on emissions from a fleet of vehicles. However vehicle-to-vehicle effects on emission levels are in general more significant than fuel quality effects, consequently prediction of emission values depend more on the vehicle technology than on the fuel. In order to illustrate fuel effects on emissions it is necessary first to remove vehicle effects as far as possible. For a particular vehicle tested on a range of different fuels, this can be achieved by calculating the mean emission value from the given fuel set for the particular vehicle, and subtracting it from each individual fuel emission value. It is then possible to compare the resultant delta emission values from several vehicles with equivalent delta emission values predicted from fleet models such as equation (1).

Different models have been used for LD-IDI (indirect injection) and LD DI (direct injection) vehicles, because of different fuel sensitivity, and for the Mercedes Benz 6L HD engine, where a different test cycle is used. The experimental data for four LD vehicles and the HD engine fuelled with SMDS and AGO samples are fully in accord with such models. This important point is exemplified for the four regulated emissions in Figs 3 and 4. In each graph delta emission values predicted from such models have been compared with the observed values for both AGO and SMDS samples.

Fig 3 compares delta emissions results from 2 IDI and 2 DI Euro II LD vehicles. SMDS samples produce lower PM, HC and CO emissions than most of the AGO fuel samples, though this effect is more marked for DI than for IDI vehicles. However, not only are the SMDS samples found close to the respective 1:1 correspondence lines for all four emissions, the linear regression line for SMDS samples alone is similar in gradient and position to the 1:1 correspondence line. This indicates that SMDS behaves predictably in the same way as AGO samples. In the case of NOx there is only very limited fuel dependence (*i.e.* NOx values are predominantly determined by engine/vehicle design), consequently SMDS produces more NOx in DI vehicles than conventional AGO in IDI ones.

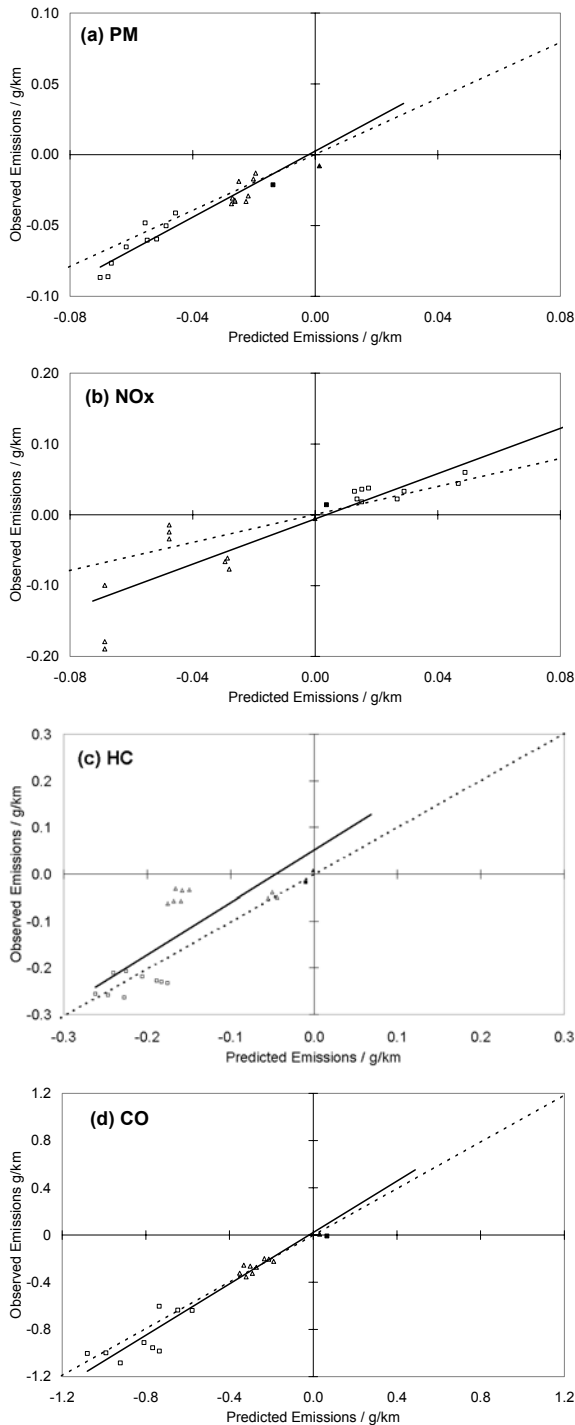


Figure 3. LD vehicles: Comparison of delta emissions values observed experimentally with those derived from models for DI and IDI vehicles. (ECE/EUDC test cycle).

(Results for SMDS (Δ IDI, □ DI) and conventional CEN AGO RF73 (▲ IDI, ■ DI) are identified, together with the 1:1 correspondence (a dotted line) and the linear regression (a continuous line) drawn through SMDS measurements alone.)

Fig 4 illustrates similar data for the Mercedes Benz 6L HD engine. In this case SMDS samples produce lower PM, HC and NOx emissions than conventional AGO. There is much less data here than for LD vehicles, nevertheless SMDS behaves as predictably as

conventional AGO for these three regulated emissions. For CO there is relatively little fuel dependence with this engine and consequently considerable scatter in the results.

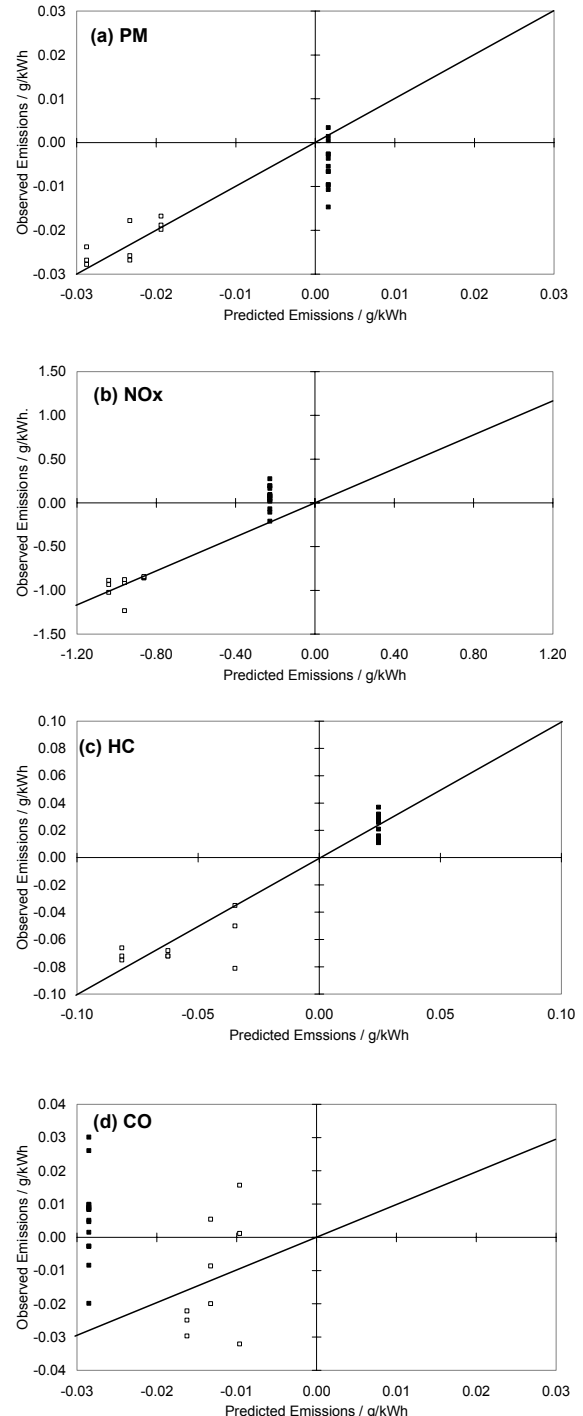


Figure 4. HD engine: Comparison of delta emissions values observed experimentally with those derived from a models (R49 test cycle).

Results for SMDS (□) and conventional CEN AGO RF73 (■) are identified, together with the 1:1 correspondence (a continuous line)

Thus the emissions performance of SMDS is well predicted by models developed for conventional diesel fuels for both LD vehicles and a HD engine. The

benefits originate primarily from the high cetane number, together with the low sulphur and low density of SMDS fuels.

4. IN-SERVICE ISSUES

There are qualifications to the use of SMDS, as its extreme properties when compared with a conventional diesel fuel, may result in some operational and compatibility concerns within engine and fuel systems.

4.1. Driver Perception

Driver perception of the effect of the very low density of the SMDS has been assessed by measurements of mass fuel consumption, volumetric fuel consumption and engine power output.

Fig 5 shows the mass and volumetric fuelling of 100% SMDS gasoil relative to current CEN AGO for four LD vehicles tuned to conventional diesel fuel. Whilst there is a small mass fuel consumption benefit (1-2%) resulting from its higher specific calorific value, there is a large detriment in volumetric fuelling (~7%), which would be perceivable to customers who of course buy on a volumetric basis. However this relative loss in volumetric fuelling will become less in the future as the density of AGO reduces to meet future diesel fuel specifications.

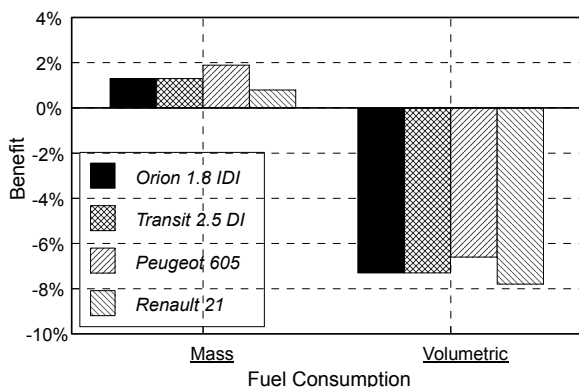


Figure 5 Fuel consumption benefits & disbenefits for 100% SMDS relative to CEN AGO (RF73).

Whilst running the tests a lack of power was noted, particularly in following the prescribed acceleration from 100 to 120 km/h in the EUDC test cycle, which is intended represent high speed driving. Similarly in HD, results from a Detroit Diesel Series 60 indicated power loss of ~10% with SMDS relative to CEN AGO during two high load modes of the R49 test cycle. For single fuel source applications (*i.e.* fleet owners), engines can be tuned to overcome some of this power loss, but the concomitant increase in volumetric fuel consumption will still remain.

4.2. Elastomer Compatibility

Elastomers are used to manufacture the seals throughout the engine fuel system. These seals form "fuel-tight" joints in both static systems (*e.g.* metal/metal joints) and

moving ones (*e.g.* rotating shafts). The performance of such seals is dependant on the elastomer properties of volume change, hardness change and flexibility change, which can be influenced by fuel composition.

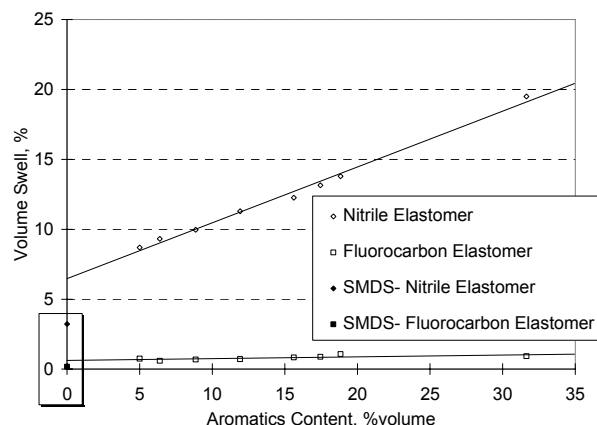


Figure 6. The linear relationship between fuel aromatic content and volume swell of various elastomers. The data for SMDS are highlighted.

(different aromatic levels achieved by blending conventional AGO with Swedish Class I)

The potential influences of low or zero aromatic fuels on seal performance have been investigated in collaboration with Original Equipment Manufacturers (OEMs)^a.⁽⁵⁾ Elastomer compatibility was assessed for SMDS and Swedish Class I fuels using measures of elastomer swell, hardness and flexibility following immersion^b with the following results:-

- The swell of an elastomer is a reversible phenomenon.
- There is an enormous difference between the swell of the nitrile seal (4-20%) and that of the fluorocarbon (0.2-1.1%).
- Within low nitrile seal experiments a clear ranking of volume swell can be seen:

CEN AGO > Swedish Class 1 > SMDS. The same ranking is apparent, but less marked, in the fluorocarbon seal and corresponds with the order of decreasing fuel aromatics content, Table 1.

- For CEN AGO and Swedish Class I fuel blends, there is a clear linear relationship between increasing total aromatics content of a fuel and increasing seal swell, Fig 6. SMDS lies well below this correlation line, *i.e.* it produces less swell than would be predicted from its lack of aromatics content.

Thus trials on SMDS showed that there was a marked reduction in nitrile elastomer swell, but fluorocarbon elastomer performances is essentially independent of

^a Fuel Injection Equipment and Elastomer manufacturers

^b using test procedures based essentially on a British Standard method BS 903 Part A 16

SMDS levels in fuel blends. Such results can be applied to make predictions about in service performance by comparison with results from Swedish Class I fuel. In this respect, the OEMs have given qualified approval to the elastomeric characteristics of Swedish class I fuel:-

- Bosch have no concern as they use the low swell fluorocarbon seals (e.g. Viton).
- Lucas have no concern, they use the nitrile capable of swell, but claim they equipment is designed not to rely on elastomer swell.

Therefore, adequate in-service performance should be achievable for SMDS if blended with conventional AGO to give a similar level of swell to that of a Swedish Class 1 (i.e. 5% swell), allowing 65-90% SMDS in a blend depending on the type of nitrile elastomer used.^c

Elastomers can be attacked by fuel peroxides. Therefore a recommendation is made that SMDS fuels are treated with an antioxidant at refinery product rundown to suppress peroxide formation. Similar recommendations have been made for Swedish Class 1, see later.

4.3. Lubricity

Lubricity is the ability of a fluid to prevent adhesive (scuffing) wear between contacting metal surfaces. This is significant because some critical components in diesel engine/fuel systems are lubricated entirely by the fuel, and problems may arise from poor fuel lubricity in rotary fuel pumps (LD vehicles) and possibly unit injectors (advanced HD engines); HD in-line fuel pumps are not thought to be sensitive.

A proven laboratory measure of lubricity which can predict in service performance is the TAFLE (Thornton Aviation Fuel Lubricity Evaluator)(6-8), which was originally designed to assess aviation fuels. There is good correlation in the assessment of AGO lubricity by the TAFLE results and field trials - the poorer lubricity fuels are those with a lower TAFLE scuffing load and lower "distance to failure" in the field trial.

The benchmark of adequate lubricity for a marketable fuel has been taken as pre-96 CEN fuel (i.e. 2000ppm S) with TAFLE scuffing loads in the region 180 - 200kg. A German field trial with full examination of the pumps has indicated that TAFLE loads of 170kg indicate adequate performance. The poor lubricity of SMDS and Swedish Class I is indicated by typical TAFLE values of 50 and 60-80 kg respectively - such values need to be increased by the use of additives or blending with conventional AGO to be fit for purpose.

Studies of the TAFLE scuffing load of SMDS or Swedish Class 1 blends with additives or pre-95 CEN

AGO show similar response curves for both fuels, [Fig 7](#). In order to achieve a scuffing load of 170kg, SMDS would need slightly more lubricity additive than Swedish Class I requires, alternatively it could be blended as a minority component with 60% pre-96 CEN AGO. However current low sulphur (<500 ppm) CEN fuel has poorer lubricity than pre-96 CEN fuel and itself needs lubricity additive, thus blending with conventional AGO is scarcely a solution to the lubricity concern.

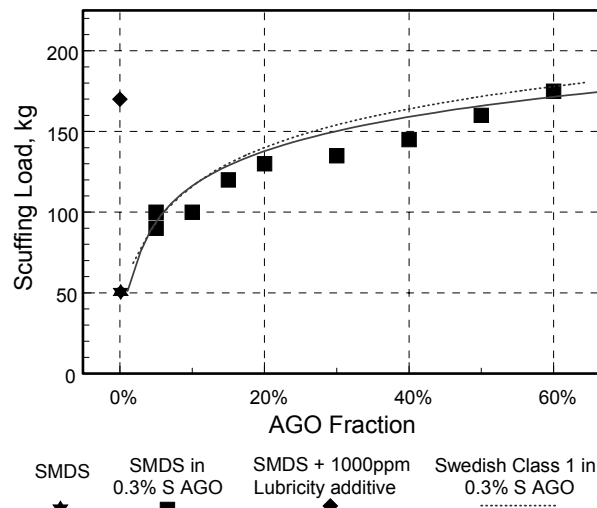


Figure 7. TAFLE scuffing loads for fuel blends

There is no field trial or HFRR^d data available for SMDS, but in any case rapid failure would be expected with those vehicles sensitive to lubricity. Based on its similarity to Swedish Class I the HFRR value for SMDS would be expected to be ~700 μm , well above the agreed CEN limit of <460 μm . However from the TAFLE data SMDS is expected to have a similar response to lubricity additive as Swedish Class I.

4.4. Stability

Traditionally the storage stability of diesel fuels has been concerned with gum and sludge formation resulting from the polar compounds present in the fuel. These unwanted products are thought to result from reactions involving polar nitrogen, sulphur and oxygen containing polar species. In this respect, it might be expected that SMDS with its low polar content performs well, and indeed the general blending behaviour of SMDS with commercial AGOs is excellent.

However, at these low levels of polar species the fuel lacks natural antioxidancy and another set of instability reactions may take over. These reactions are essentially uninhibited oxidation of the fuel, resulting in peroxides, acids and insoluble product precursors. Thus in terms of stability, SMDS would need the addition of antioxidants at refinery product rundown to suppress peroxide formation.

^c This limit of SMDS in AGO has been set with respect to an elastomer compatibility issue, other criteria will result from other fuel properties, e.g. lubricity, power and volumetric fuelling.

^d HFRR = High frequency reciprocating rig in European test CEC F-06-A-96 used internationally to assess AGO lubricity

4.5. Cold Flow Performance

Diesel fuel needs to flow freely through filters at low ambient operating temperatures otherwise fuel starvation will result. Filter blocking can occur as a result of the formation of wax crystals formed from higher paraffins usually present in AGO, and in general highly paraffinic AGO samples have poor cold flow characteristics. There are potential performance trade-offs here for increasing iso-alkanes in SMDS which would improve the cold flow behaviour but may lead to poorer cetane quality.

Cold flow performance is assessed from a knowledge of the cloud point (CP), pour point (PP) and cold flow plugging point (CFPP) of the sample, and the minimum temperature limit of operability can be calculated from an empirical relationship based on CP and CFPP. Additives have been developed to improve cold flow behaviour by modifying wax crystallisation to give much smaller and differently shaped crystals which are kept in suspension [8], and these are commonly used for winter fuel grades.

Typical cold flow temperature ranges for SMDS are +4°C to -6°C, whether CP, CFPP or PP, and these values become higher (i.e. worse) with increasing average carbon number. Whilst these temperatures are not unusually high in themselves, unfortunately SMDS has been found to be unresponsive to cold flow additives, and the typical requirement for CFPP in Central European winter grades is below -20°C and below. There is potential however to introduce process modifications which would reduce CFPP to significantly lower temperatures, e.g. -15°C. Nevertheless cold flow properties may constrain the use of SMDS as a stand-alone automotive fuel, except in niche markets. However in AGO blends containing up to 30% SMDS the responsiveness to CFPP improves remains largely intact.

4.6. Biodegradability

Although there have been no direct measurements of the biodegradability of the SMDS diesel cut, it can readily be inferred from its chemical composition that the biodegradation of SMDS will be much faster than conventional AGO. This is because the ease of biodegradability of hydrocarbons decreases in the order straight-chain paraffins < branched alkanes < cycloparaffins (naphthenes) < aromatics (9). Thus from their differences in aromatics and paraffin contents one would expect biodegradability to improve in the order: conventional AGO < Swedish Class I < SMDS, i.e. SMDS is the most easily biodegradable.

5. CONCLUSIONS

Although SMDS exhibits significant emission benefits compared with conventional AGO, this is offset by a range of in-service disbenefits. Its elastomer compatibility and cold flow performance are of

sufficient concern to limit its use primarily to that of a blending component for AGO. Thus its benefits:-

- Good emissions performance of SMDS originating from its high cetane number, low sulphur and low density, and is predicted by models developed for conventional diesel fuels for both LD vehicles and HD engines. Its emission benefits over current CEN AGO are :-
 - a) LD vehicles - PM, HC and CO lowered by 40-50%, NOx reduced by 5-10%,
 - b) HD engines - PM, NOx, HC and CO all reduced by 15-20%.
- Better biodegradability than for conventional AGO.

are offset by several disadvantages:-

- The relative lack of elastomer swelling from SMDS compared with conventional fuels could potentially cause problems in-service, because of potential seal deterioration unless blended with 10-35% conventional AGO. However this may be overcome by future specific engine developments.
- SMDS is unresponsive to cold flow additives unless being used as a minor blend component (<30%) in AGO. However it may be possible to develop an additive specific to SMDS or mitigate the problem by targeted processing.
- Some power loss and ~7% loss in volumetric fuel consumption would be perceived by drivers of conventional diesel vehicles when switching from standard AGO to 100% SMDS.
- Although rapid failure would be expected with those vehicles with fuel pumps sensitive to lubricity when operating with SMDS alone, its HFRR response to lubricity additives is quite satisfactory.
- Antioxidants are necessary to protect elastomers from fuel peroxides, and to safeguard fuel stability.

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